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U.S. PTO

Donna F. Maines  
(Mailer)

## DIVISION APPLICATION TRANSMITTAL FORM

ATTORNEY'S DOCKET NO.  
PD-30-3986DIV(4510)

DOCKET NUMBER:

PD 30-3986DIV(4510)

ANTICIPATED CLASSIFICATION OF THIS APPLICATION:

CLASS:  
570

SUBCLASS:

PRIOR APPLICATION:

08/530,649

EXAMINER:

M. Cebulak

ART UNIT:

1209

## To the Assistant Commissioner for Patents:

This is a request for filing a ☒ divisional application under 37 CFR 1.60, of pending prior application

serial no. 08/530,649 filed on September 20, 19 95, of

Clemmer et al. for Process for the Production of Difluoromethane

1. ☒ Enclosed is a copy of the latest inventor signed prior application, including the oath or declaration as originally filed. I hereby verify that the attached papers are a true copy of the latest inventor signed prior application serial no. 08/530,649 as originally filed on September 20, 19 95, and further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.
2. ☒ Cancel in this application original claims 10-18 of the prior application before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
3. ☒ The filing fee is calculated below.

FOR	NUMBER FILED	NUMBER EXTRA	RATE	FEE
TOTAL CLAIMS	15- 20 =	0	x \$22 =	
INDEPENDENT CLAIMS	3- 3 =	0	x \$82 =	
			BASIC FEE	\$790.00
Multiple dependent claims \$ 270.00			TOTAL FILING FEE	\$1060.00

4. ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment, to Deposit Account No. 01-1125. A triplicate copy of this sheet is enclosed.
5. ☒ Amend the specification by inserting before the first line the sentence: This application is a ☒ division of application serial no. 08/530,649, filed September 20, 1995.

6. ☐ Transfer the drawings from the pending prior application to this application and abandon said prior application as of the filing date accorded this application. A duplicate copy of this sheet is enclosed for filing in prior application file. (May only be used if signed by person authorized by § 1.138 and before payment of base issue fee.)

a. ☐ New formal drawings are enclosed.

b. ☐ Priority of application serial no. \_\_\_\_\_ filed on \_\_\_\_\_ in

\_\_\_\_\_ is claimed under 35 U.S.C. 119.  
(country)

☐ The certified copy has been filed in prior application serial no. \_\_\_\_\_  
filed \_\_\_\_\_.

7. ☒ The prior application is assigned of record to AlliedSignal Inc.

8. ☐ A preliminary amendment is enclosed.

9. ☐ Also enclosed \_\_\_\_\_

10. ☒ The power of attorney in the prior application is to Lois A. Gianneschi 35,519  
Jay P. Friedenson 22,465

a. ☒ The power appears in the original papers in the prior application.

b. ☐ Since the power does not appear in the original papers, a copy of the power in the prior application is enclosed.

c. ☐ Address all future communications: (May only be completed by applicant, or attorney or agent of record)

Lois A. Gianneschi

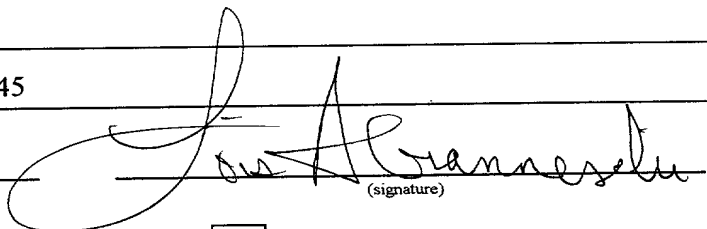
AlliedSignal Inc.

Law Department

PO Box 2245

Morristown, New Jersey 07962-2245

October 28, 1997  
(date)

  
(signature)

Identity of signator:

☐

inventor(s)

☐

filed under § 1.34(a)

☐

assignee of complete interest

☒

attorney or agent of record

PD 30-3986 (4510)

## PROCESS FOR THE PRODUCTION OF DIFLUOROMETHANE

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### Field of the Invention

The present invention relates to a vapor phase process for the production of difluoromethane, HFC-32. In particular, this invention provides a process for the preparation of HFC-32 that exhibits good product yield and selectivity.

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### Background of the Invention

It is well known in the art that HFC-32 may be used as a replacement for environmentally disadvantageous chlorofluorocarbon refrigerants, blowing agents, and aerosol propellants. A variety of methods for the vapor phase production of HFC-32 are known.

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For example, US Patent No. 2,745,886 discloses a vapor phase process for fluorinating a variety of halohydrocarbons including methylene chloride, HCC-30, which process utilizes a hydrated chromium fluoride catalyst activated with oxygen. Similarly, US Patent No. 2,744,148 discloses a halohydrocarbon fluorination process in which an HF-activated alumina catalyst is used.

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US Patent No. 3,862,995 discloses the vapor phase production of HFC-32 by reacting vinyl chloride and HF in the presence of a vanadium derivative catalyst supported on carbon. US Patent No. 4,147,733 discloses a vapor phase reaction for the production of HFC-32 by HCC-30 with HF in the presence of a metal fluoride catalyst.

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In practice, these processes for HFC-32 production suffer from a variety of problems including low product yield and selectivity as well as operational

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difficulties such as feed decomposition. The process of this invention provides for the production of HFC-32 by a process that overcomes some of the disadvantages of the known processes.

5                   Description of the Invention and Preferred Embodiments

The present invention provides a method for HFC-32 production in good yield and selectivity. In general, the process of this invention comprises contacting HCC-30 and HF in the presence of a fluorination catalyst to produce a product stream of difluoromethane, chlorofluoromethane ("HCFC-31"), hydrogen  
10   chloride, dichloromethane, and hydrogen fluoride and separating HFC-32 from the product stream. In a preferred embodiment, the invention comprises the steps of:

(A) preheating a composition comprising hydrogen fluoride ("HF") and HCC-30 and, optionally, HCFC-31, to form a vaporized and superheated  
15   composition;

(B) reacting the preheated composition of step (A) in the presence of a fluorination catalyst under conditions suitable to form a product stream comprising HFC-32, HCFC-31 and hydrogen chloride and unreacted HCC-30 and HF;

(C) recovering by distillation from the product stream of step (B) a high  
20   boiling fraction comprising HF, HCC-30, and HCFC-31 and a low boiling fraction comprising HFC-32, HCl, HF, and reaction byproducts; and

(D) recovering substantially pure HFC-32 product from the low boiling fraction of step (C).

25           In step (A) a composition comprising HF and HCC-30 is preheated in at least one vaporizer. By "preheating" is meant to vaporize and superheat the composition. The composition is heated to a temperature of from about 125° C to about 400° C, preferably 150° C to about 300° C, more preferably from about 175° C to about 275° C and most preferably 200° C to about 250° C. The

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vaporizer, as well as the other vessels used in this process, may be made of any suitable corrosion resistant material.

Although fresh HF and HCC-30 may be used in step (A), preferably the composition of step (A) contains recycled material from step (C) as described below. When the process is run without continuous recycle, the mole ratio of HF to organic, specifically the mole ratio of HF to HCC-30, is from about 1:1 to about 10:1, preferably from about 1:1 to about 4:1. Optionally, fresh HCFC-31 may be added to the composition of step (A).

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Alternatively, a continuous recycle stream of the high boiling fraction obtained in step (C) is recycled to step (A) in which case a large excess of HF to organics is used. In the process of this invention, the higher the HF:organics mole ratio, the higher the yield and selectivity for HFC-32. Correspondingly, a large excess of HF will result in the reduction of HCFC-31 produced as well as the concentration of unreacted HCC-30. Additionally, the use of a large excess of HF will decrease catalyst deactivation rates and result in less decomposition in preheaters and vaporizers, especially when the reaction is conducted at pressures in excess of 3 atmospheres. Generally, a ratio of HF to HCFC-31, as measured after separation of HFC-32 from the product stream, of at least about 25:1 to at least about 300:1, preferably at least about 50:1 to at least about 200:1, and more preferably at least about 75:1 to at least about 150:1 is used.

The preheated composition of step (A) is reacted in step (B) in a vapor phase fluorination reaction to form a product stream mixture. The reaction may proceed in one or more isothermal or adiabatic reactors. When more than one reactor is used, the reactor arrangement is not critical, but a sequential arrangement is preferred. Inter-reactor heating or cooling may be used to obtain the best reactor performance.

The reactor or reactors used in this process are filled with a fluorination catalyst and the organic and HF vapor is allowed to contact the catalyst under conditions suitable to form a reaction mixture. The reactor temperature is maintained at from about 125° to about 425° C, preferably 150° C to about 300° C, more preferably 175° C to about 275° C and most preferably 200° C to about 250° C. Reactor pressure may be atmospheric, subatmospheric, or superatmospheric. Preferably reactor pressure is maintained at from about 0 psig to about 250 psig. Contact time, the time required for the reactants to pass through the catalyst bed assuming a 100% void catalyst bed, is typically from about 1 to about 120 seconds, preferably from about 2 to 60 seconds, more preferably from about 4 to about 50 seconds, and most preferably from about 5 to about 30 seconds.

Any known vapor phase fluorination catalyst may be used in the process of this invention. Exemplary catalysts include, without limitation, chromium, copper, aluminum, cobalt, magnesium, manganese, zinc, nickel and iron oxides, hydroxides, halides, oxyhalides and inorganic salts thereof,  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{AlF}_3$ ,  $\text{Cr}_2\text{O}_3/\text{carbon}$ ,  $\text{CoCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{NiCl}_2/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{CoCl}_2/\text{AlF}_3$  and  $\text{NiCl}_2/\text{AlF}_3$ . Additionally, supported metal catalysts such as nickel, cobalt, zinc, iron, and copper supported on chromia, magnesia, or alumina may be used. Chromium oxide/aluminum oxide catalysts are described in US Patent No. 5,155,082 which is incorporated herein in its entirety. Preferably, chromium oxide, a commercially available catalyst, is used. The chromium oxide may be crystalline or amorphous. Preferably, amorphous chromium oxide is used. The catalyst is used in an amount effective to drive the reaction.

The fluorination catalyst may be, and is preferably, pretreated prior to the introduction of the reaction feed stock. By "pretreat" is meant to chemically or

physically alter the catalyst in order to create active sites on the catalyst at which the reaction may occur. The catalyst is pretreated by calcining under a flow of inert gas such as nitrogen at a temperature from about 200° C to about 450° C for at least about 1 hour. The catalyst is then exposed to HF alone or in combination  
5 with up to about 5 to about 99 weight percent of an inert gas at a temperature from about 200° C to about 450° C for at least about 1 hour. Preferably, the catalyst then undergoes a third pretreatment step in which it is contacted with chlorine gas. Preferably, the chlorine is diluted with from about 60 to about 75 % HF and/or from about 20 to about 30 % of an inert gas. The chlorine may be  
10 passed over the catalyst at a total volume chlorine to total volume catalyst of about 1: 3,000 v/v, preferably about 10:1,000 v/v, more preferably about 50:500 v/v. Exposure time may be from about 1 to about 200 hours, preferably 5 to 70 hours, more preferably 10 to 30 hours. The chlorine exposure may be conducted at any temperature and pressure convenient to the fluorination reaction.

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The flow of chlorine is discontinued after pretreatment is complete and the feed HF and HCC-30 introduced. A small amount of chlorine, from about 0.1 to about 10 mol percent based on organic content, preferably from about 2 to about 8 mol percent, may be added to the reactor, preferably while the fluorination reaction  
20 proceeds, for periods of time from about 1 to about 200 hours, preferably from about 5 to about 70 hours, and more preferably from about 10 to about 25 hours, should the catalyst become deactivated to restore activity.

The product stream produced in step (B) contains reaction products which  
25 are HFC-32, HCFC-31, and HCl as well as unreacted feed stock such as HF and HCC-30. The product stream of step (B) is fed into a recycle column in step (C). The recycle column may be any standard distillation column known in the art. The high boiling fraction, or bottom stream, from the recycle column is composed of unreacted HF and HCC-30 and intermediate reactant HCFC-31. Preferably, this

mixture is recycled to step (A) after recovery. Further in step (C), a low boiling fraction, or top stream, of HFC-32, HCl, HF, and reaction byproducts is recovered.

- 5           Alternatively, step (C) may be performed in two parts. In the first part, the product stream of step (B) is quenched. By "quenching" is meant that the temperature of the reaction mixture is reduced to below its dew point. Quenching may be conducted in a packed column containing any suitable corrosion resistant packing material and a suitable refluxing liquid such as HF, HCC-30, and/or
- 10   HCFC-31 after which the quenched product is fed into the recycle column.

- In step (D), substantially pure HFC-32 is recovered from the low boiling fraction of step (C) by any method well known in the art. Preferably step (D) is performed by a series of substeps including step (E), treating the gaseous mixture
- 15   in an HCl distillation column or aqueous HCl absorption tower under conditions suitable to remove HCl and trace HF. The crude HFC-32 product of step (E) is then treated in step (F) with a first caustic scrubber under conditions suitable to form a neutralized product by neutralizing residual acidity. Typically, the caustic scrubber contains water, sodium hydroxide, or potassium hydroxide. Step (F) is
- 20   followed by step (G) in which the step (F) product is treated in a second caustic scrubber, preferably comprising sodium hydroxide together with a sulfite, such as sodium sulfite under conditions suitable to remove residual chlorine and form a substantially chlorine-free product. In step (H), the step (G) product is treated with a sulfuric acid scrubber followed by a solid desiccant, such as any suitable,
- 25   commercially available, molecular sieve that absorbs residual moisture from the gas stream to form a substantially moisture-free product. This is followed by step (I) in which the step (H) product is conducted through a plurality of distillation columns under conditions sufficient to remove the residual impurities and produce

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substantially pure HFC-32, greater than 99.97 weight percent. Any residual HCFC-31 removed in step (I) may be recycled to step (A).

The following non-limiting examples will serve to clarify and exemplify the process of this invention.

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#### Examples 1 and 2

In a 1/2 inch Monel pipe reactor, about 110 ml  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  (40/60 wt %) co-extruded catalyst were packed. The catalyst was dried/calined at about 400° C for about 16 hours using air at 2-3 liters per minute. Then, the temperature was  
10 lowered to 200° C and air was replaced with nitrogen at about 0.5 - 1.5 liters per minute. Anhydrous HF was pumped into the reactor at about 1-2 ml/min until exotherm passed through the reactor. Subsequently, temperature was raised at 25° C every half hour until the temperature was about 350 - 400° C and held there for 8 hours. Temperature was then lowered to the desired reaction temperature.  
15 HF and HCC-30 were fed into the reactor at a molar ratio of 4:1 (HF:HCC-30). The mixture of HF and HCC-30 passed through two preheaters, the first of which was at about 100 - 185° C and the second at about 200 - 275° C. The pressure was 50 psig and reactor temperature was 275° C for Example 1 and 300° C for Example 2. For Example 1, contact time was 16 seconds resulting in 82 %  
20 conversion and 89.3 % HFC-32 selectivity. The productivity was 10 lbs HFC-32/hr/ft<sup>3</sup>. Contact time for Example 2 was 10 seconds and HCC-30 conversion decreased to 77 %. HFC-32 productivity for Example 2 was 13.6 lbs/hr/ft<sup>3</sup> and HFC-32 selectivity was about 85 %. The results of these examples are summarized on Table I.

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Table I

	Example 1	Example 2
Catalyst	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (40/60 wt %)	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (40/60 wt %)
Pressure	50 psig	50 psig
HF/HCC-30	4	4
Temperature °C	275	300
Contact Time (sec.)	16	10
Conversion % CH <sub>2</sub> Cl <sub>2</sub>	82	77
Selectivity (%):		
HFC-32	89.3	84.7
HCFC-31	10.6	15.2
HCC-40	0.1	0.1
Productivity (lbs/hr/ft <sup>3</sup> ):		
HFC-32	10.3	13.6

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### Examples 3 - 6

In the pipe reactor of Examples 1 and 2, about 100-110 ml Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst of 78/22 weight percent ratio was packed. The catalyst was dried/calcined and HF-treated using the same procedure as for Examples 1 & 2. HF and HCC-30 were fed into the reactor at a 4:1 (HF/HCC-30) ratio. A mixture of HF and HCC-30 was passed through the same preheaters indicated in Examples 1 & 2. Pressures, contact times, and the results are shown on Table II.

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Table II

	Example 3	Example 4	Example 5	Example 6
Catalyst	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (78/22 wt %)	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (78/22 wt %)	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (78/22 wt %)	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (78/22 wt %)
Pressure (psig)	50	200	225	225
HF/CH <sub>2</sub> Cl <sub>2</sub> mole ratio	4	4	4	4
Temperature (°C)	275	275	275	275
Contact Time (sec)	11	36	40	26
Conversion (% CH <sub>2</sub> Cl <sub>2</sub> )	71	70	70	61
Selectivity:				
HFC-32	82	81	81	77
HCFC-31	18	19	19	23
HCC-40	0.05	0.05	0.05	0.05
Productivity (lbs/hr/ft <sup>3</sup> ):				
HFC-32	12	12	12	15

### Example 7

- A 4 inch diameter Monel 400 reactor was charged with 4 liters of
- 5 chromium oxide catalyst. The catalyst was dried under 20 slpm nitrogen flow at a temperature of 350° C for 8 hours. After reducing the catalyst bed temperature to 250° C, anhydrous HF was added to the flowing nitrogen at a flow rate of 0.2 lbs/hr. The HF flow rate was gradually increased to 1.0 lb/hr and the temperature increased to 350° C and held for 4 hours. The catalyst bed temperature was then

decreased to 250° C and chlorine introduced to the HF/N<sub>2</sub> mixture at a rate of 500 sccm for a period of 24 hours.

After this pretreatment procedure, the chlorine and nitrogen flows were discontinued and HCC-30 was mixed with HF and passed through a preheater at 185° C. The vaporized HCC-30 and HF mixture was fed to the reactor at a pressure of 45 psig. the effluent from the reactor was quenched using a heat exchanger and fed into a distillation column maintained at 50 psig. The low boiling distillation components, HCFC-31, HF, and HCC-30 were recycled back to mix with fresh HF and HCC-30 feed stream and were fed to the preheater, and the reactor at a flow rate of 4.6 lbs/hr. The recycle stream contained a molar ratio of HF : HCFC-31 of 360 :1. The recycle material was mixed with additional HF and HCC-30 at flow rates of 0.5 and 1.0 lbs/hr, respectively, before being passed over the catalyst. The resulting contact time was 12 seconds. The low boiling components separated in the distillation column, HCl and HFC-32, were passed through a caustic scrubber containing 10 % KOH where HCl was removed. The purified HFC-32 was dried and collected. The resulting HCC-30 conversion was 90 % with 90 % selectivity to HFC-32 and 9 % selectivity to HCFC-31.

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What is claimed is:

- 5 1. A process for the production of difluoromethane comprising:
  - (a) contacting dichloromethane with hydrogen fluoride in the presence of a fluorination catalyst to produce a product stream of difluoromethane, monochloromonofluoromethane, and unreacted starting materials and
  - (b) separating difluoromethane from the product stream from step (a)
- 10 wherein sufficient hydrogen fluoride is employed in the process such that during step (b) the molar ratio of hydrogen fluoride to monochloromonofluoromethane is at least about 100:1.
2. A process as claimed in claim 1, in which the molar ratio of hydrogen
- 15 fluoride to monochloromonofluoromethane is at least about 150:1.
3. A process as claimed in claim 1 in which additional hydrogen fluoride is added to the process stream recovered from step (a) in order to ensure that the required ratio of hydrogen fluoride to HCFC-31 is achieved during step (b).
- 20 4. A process for the production of difluoromethane comprising (a) contacting dichloromethane with hydrogen fluoride in the presence of a fluorination catalyst to produce a product stream comprising difluoromethane, monochloromonofluoromethane and unreacted starting materials, (b) separating
- 25 difluoromethane from the product stream from step (a) and (c) recovering difluoromethane and recycling HCFC-31 to step (a) wherein sufficient hydrogen fluoride is employed in the process such that during step (b) the molar ratio of hydrogen fluoride to monochloromonofluoromethane is at least about 100:1.

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5. A process as claimed in any one of claims 1 to 4 in which the separation step (b) comprises distilling the product stream from step (a) whereby to separate a top stream comprising difluoromethane and hydrogen chloride from a bottom stream comprising hydrogen fluoride, HCFC-31 and unreacted dichloromethane.

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6. A process as claimed in any one of claims 1 to 5 in which the fluorination catalyst comprises a metal oxide, metal fluoride or oxyfluoride.

7. A process as claimed in claim 6 in which the metal of the oxide, fluoride, or oxyfluoride is at least one of chromium, aluminum, zinc, nickel, cobalt, copper and magnesium.

8. A process as claimed in claim 7 in which the catalyst comprises zinc or a compound of zinc and a metal oxide, fluoride or oxyfluoride in which the metal of the oxide, fluoride or oxyfluoride is chromium or aluminum.

9. A process for producing difluoromethane comprising the steps of:  
(A) preheating a composition comprising hydrogen fluoride and dichloromethane to form a vaporized and superheated composition;  
(B) reacting the preheated composition of step (A) in the presence of a fluorination catalyst under conditions suitable to form a product stream comprising difluoromethane, chlorofluoromethane, hydrogen chloride, dichloromethane and hydrogen fluoride;  
(C) recovering by distillation from the product stream of step (B) a high boiling fraction comprising hydrogen fluoride, dichloromethane, and chlorofluoromethane and a low boiling fraction comprising difluoromethane, hydrogen chloride, hydrogen fluoride, and reaction byproducts; and  
(D) recovering substantially pure difluoromethane from the low boiling fraction of step (C).

10. The process of claim 9 wherein the hydrogen fluoride and dichloromethane are present in a mole ratio of from about 1:1 to about 10:1.

5 11. The process of claim 9 wherein the composition of step (A) further comprises chlorofluoromethane.

12. The process of claims 9 or 11 wherein the hydrogen fluoride and the chlorofluoromethane are present in the product stream in a mole ratio of at least  
10 about 25:1 to at least about 300:1.

13. The process of claims 9 or 11 wherein the hydrogen fluoride and the chlorofluoromethane are present in the product stream in a mole ratio of at least  
15 about 50:1 to at least about 200:1.

14. The process of claims 9 or 11 wherein the hydrogen fluoride and the chlorofluoromethane are present in the product stream in a mole ratio of at least  
about 75:1 to at least about 150:1.

20 15. The process of claims 1 or 9 wherein the fluorination catalyst is a pretreated fluorination catalyst

16. The process of claims 1, 9 or 15 wherein the fluorination catalyst is chromium oxide.

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17. The process of claim 9 wherein the high boiling fraction of step (C) is recycled to step (A).

18. The process of claim 9 wherein step (D) further comprises the substeps of:

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(E) treating the low boiling mixture of step (C) in an HCl distillation column or an aqueous HCl absorption tower under conditions suitable to remove HCl and trace HF to form a crude HFC-32 product;

(F) treating the crude HFC-32 product formed in step (E) with a first  
5 caustic scrubber under conditions suitable to form a neutralized product;

(G) treating the neutralized product of step (F) in a second caustic scrubber under conditions suitable to form a substantially chlorine-free product;

(H) treating the substantially chlorine-free product of step (G) with a sulfuric acid scrubber and subsequently with a solid desiccant to form a substantially moisture-free product; and

(I) distilling the substantially moisture-free product of step (H) under conditions suitable to produce substantially pure difluoromethane.

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Abstract of the Invention

The present invention provides a vapor phase process for the production of difluoromethane, HFC-32. The process of this invention provides for the  
5 preparation of HFC-32 by a process that exhibits both good product yield and selectivity.

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# DECLARATION FOR PATENT APPLICATION SOLE OR JOINT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention titled:

## PROCESS FOR THE PRODUCTION OF DIFLUOROMETHANE

the specification of which can be identified as U.S. Patent Application Serial No 08/530,649 filed September 30, 1995.

I HEREBY STATE THAT I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS.

I ACKNOWLEDGE THE DUTY TO DISCLOSE INFORMATION THAT IS MATERIAL TO THE PATENTABILITY OF THIS APPLICATION IN ACCORDANCE WITH TITLE 37, CODE OF FEDERAL REGULATIONS, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

### Prior Foreign Application(s)

			Priority Claimed	
(Number)	(Country)	(Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
_____	_____	_____	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
_____	_____	_____	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States applications listed below and, INsofar AS THE SUBJECT MATTER OF EACH OF THE CLAIMS OF THIS APPLICATION IS NOT DISCLOSED IN THE PRIOR UNITED STATES APPLICATION IN THE MANNER PROVIDED BY THE FIRST PARAGRAPH OF TITLE 35, UNITED STATES CODE, §112, I ACKNOWLEDGE THE DUTY TO DISCLOSE MATERIAL INFORMATION AS DEFINED IN TITLE 37, CODE OF FEDERAL REGULATIONS, §1.56(a) WHICH OCCURRED BETWEEN THE FILING DATE OF THE PRIOR APPLICATION AND THE NATIONAL OR PCT INTERNATIONAL FILING DATE OF THIS APPLICATION:

\*\*

08/530,649	September 20, 1995	Pending
(Application Serial Number)	(Filing Date)	(STATUS: Patented, Pending, Abandoned)
_____	_____	_____
(Application Serial Number)	(Filing Date)	(STATUS: Patented, Pending, Abandoned)

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected herewith (List name and registration number).

(LIST SENIOR PATENT COUNSEL AND ATTORNEY HANDLING CASE WITH PATENT OFFICE REGISTRATION NUMBERS.)

Lois A. Gianneschi	Jay P. Friedenson	_____
Name	Name	Name
35,519	22,465	_____
Registration Number	Registration Number	Registration Number

SEND CORRESPONDENCE TO:

Lois A. Gianneschi

AlliedSignal Inc.

P.O. Box 2245

101 Columbia Road, Morristown, New Jersey 07962

DIRECT TELEPHONE CALLS TO:

Lois Gianneschi (201) 455-3679

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

FULL NAME OF SOLE OR FIRST INVENTOR Paul Gene ClemmerINVENTOR'S SIGNATURE Paul Gene ClemmerDate June 25, 1997RESIDENCE Williamsville, Erie County, State of New YorkCITIZENSHIP United States of AmericaPOST OFFICE ADDRESS 128 Royal Parkway WestWilliamsville, NY 14221FULL NAME OF SECOND JOINT INVENTOR Addison Miles SmithINVENTOR'S SIGNATURE Addison Miles SmithDate June 25, 1997RESIDENCE Amherst, Erie County, State of New YorkCITIZENSHIP United States of AmericaPOST OFFICE ADDRESS 80 Berryman DriveAmherst, NY 14226FULL NAME OF THIRD JOINT INVENTOR Hsueh Sung TungINVENTOR'S SIGNATURE Hsueh Sung TungDate June 26, 1997RESIDENCE Getzville, Erie County, State of New YorkCITIZENSHIP United States of AmericaPOST OFFICE ADDRESS 16 Vassar DriveGetzville, NY 14068FULL NAME OF FOURTH JOINT INVENTOR John Stephen BassINVENTOR'S SIGNATURE John Stephen BassDate June 25, 1997RESIDENCE East Amherst, Erie County, State of New YorkCITIZENSHIP United States of AmericaPOST OFFICE ADDRESS 327 Greengage CircleEast Amherst, NY 14051

FULL NAME OF FIFTH JOINT INVENTOR \_\_\_\_\_

INVENTOR'S SIGNATURE \_\_\_\_\_

Date \_\_\_\_\_

RESIDENCE \_\_\_\_\_

CITIZENSHIP \_\_\_\_\_

POST OFFICE ADDRESS \_\_\_\_\_

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